EFFECT OF DIFFERENT TYPE OF POLYMER CONCENTRATION ON ASYMMETRIC POLYSULFONE MEMBRANE FOR CO_2/CH_4 SEPARATION

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ABSTRACT

The objective of this study is to developed polysulfone (PSU) asymmetric membrane for gas separation and to identify the concentration of polysulfone in dope solution to produce high selectivity membrane for CO_2/CH_4 gas separation. Polysulfone was selected as the polymer material in this research since it is glassy type polymer that exhibit good mechanical properties compare to others while 1-Methyl-2-Pyrrolidone (NMP) is chosen as the solvent because it is low toxicity and completely miscible with water, organic acid and alcohol. Polysulfone asymmetric membrane was prepared by mixing a dope, where polysulfone polymer was mixed with 1-Methyl-2-Pyrrolidone (NMP). Three sample of solution was prepared with different type of concentration of polysulfone polymer which is 20 wt%, 25 wt% and 30 wt% respectively. Before perform gas permeation test, polysulfone membrane was coating with PDMS and n-hexane with the composition 3 wt% and 97 wt% respectively. Permeation test was carried out by using single gas permeation test by testing gas carbon dioxide (CO_2) and methane (CH_4). The membranes were characterized by using Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). Through SEM analysis, the morphology and structure of the membrane at 20 wt% concentration of polysulfone shows structural pores using 1000 magnification. Membranes with 30 wt% of PSU exhibits the most selective membrane with selectivity about 2.619 while membrane with 20 wt% shows the lowest selectivity that is 1.22. This is because the increasing polysulfone polymer concentration resulted a denser and thicker skin layer of membrane so that the membrane with high polysulfone concentration become more selective but less permeability to the gas separation.

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan membrane asimetrik polysulfone untuk tujuan pengasingan gas CO_2/CH_4 dan untuk mengenal pasti kepekatan polymer yang dapat menunjukkan ciri-ciri selektif yang paling baik. Polysulfone dipilih sebagai material untuk polymer dalam penghasilan membrane kerana ia menunjukkan ciri-ciri mekanikal yang baik berbanding polymer lain manakala 1-Methyl-2-Pyrrolidone (NMP) dipilih sebagai pelarut kerana ianya kurang toksid dan dapat terlarut sepenuhnya bila bergabung dengan air. Membrane asimetrik Polysulfone disediakan dengan mencampurkan larutan dope, dimana polysulfone dicampur bersama 1-Methyl-2-Pyrrolidone (NMP). Tiga jenis sampel untuk larutan disediakan pada kepekatan polymer yang berbeza iaitu masing masing 20 wt%, 25 wt% and 30 wt% . Sebelum menjalankan ujian penyerapan gas, polysulfone membrane dilapisi menggunakan PDMS and n-hexane dengan kandungan material masing-masing 3 wt% and 97 wt%. Ujian penyerapan gas dijalankan menggunakan alat ujian penyerapan gas dengan menguji gas karbon dioksida (CO_2) dan methane (CH_4). Kesemua membrane menjalani ujian menggunakan Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) untuk melihat struktur membrane. Melalui analysis SEM, struktur membrane pada kepekatan polysulfone 20 wt% menunjukkan struktur kaviti yang besar pada magnifikasi 1000. Membrane dengan kepekatan polymer 30 wt% menunjukkan ciri yang paling selektif dengan nilai selektiviti 2.619 manakala membrane dengan kepekatan 20 wt% menunjukkan selektiviti paling rendah iaitu pada 1.22. Hal ini kerana penambahan kepekatan polymer menyebabkan struktur membrane menjadi semakin padat dan tebal dan menyebabkan membrane menjadi semakin selektif.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

In natural gas processing, it involved the separation of some of the components contain in natural gas such as water, acid gas and heavy carbon in order to satisfy the commercial specifications. Carbon dioxide (CO_2) which falls into category of acid gases is commonly found in natural gas stream at level as high as 80 percent. In combination with water, it is highly corrosive and rapidly destroys pipeline and equipment unless it is particularly removed or expensive construction materials are used. Carbon dioxide reduces the heating value of natural gas. In LNG plant, carbon dioxide must be removed to prevent freezing in low temperature chiller.

There are various types of acid gas removal process such as solvent absorption, solid adsorption, direct conversion, cryogenic fractionators and membranes. This research will focus on membranes separation process.

The membrane processes have the some characteristic as the alternative technology. According to Baker (2000), membrane technology is continuity and simplicity process compared to conventional separation technology. Besides, this technology is flexibility in designed because it can be combined with each other and with other separation technologies to meet complex demand in separation technology. The other characteristic of membrane technologies that give significant advantages to the industries is the compactness of it design that suitable for the plant that limited in area.

At the moment, the most widely used membrane materials for gas separation are polymers. Polysulfone (PSU) was chosen as the polymer for this study since it is used commercially as a gas separation membrane material, and its gas transport properties have been extensively studied (Ahn *et al*., 2008).

This research will be concentrate about effect of polymer concentration on the development of polysulfone membrane for acid gas removal.

1.2 PROBLEM STATEMENT

The separation of carbon dioxide from methane is one of the important processes in many industrial areas such as natural gas processing, biogas purification, enhanced oil recovery and flue gas treatment. Carbon dioxide in natural gas must be removed because it causes pipe corrosion, reduces the heating value, takes up volume in the pipeline and is able to solidify in cryogenic process. Besides, being a greenhouse gas, the emission of carbon dioxide from the combustion of fossil fuel is a serious concern associated with global climate change. Conventional absorption processes are generally operated in the contactor devices, example, packed and plate columns, which require huge space and high investment cost. In addition, they also suffer from several operational limitations including flooding, entrainment and foaming. Membrane gas permeation process is an alternative separation process for capturing carbon dioxide, but low gas flux and methane loss are the two main problems in gas permeation process. Thus, it is imperative to develop more efficient processes for upgrading low quality gases than presently available ones.

Typically, polymers which are highly permeable to gases have low permselectivity and vice versa. It is hard to find high performances with both selectivity and permeability. Most of membranes selectivity is inversely proportional with permeability (Ridzuan *et al*., 2004). Studies on the relationship between polymer materials and gas separation properties were carried out to understand membrane permeability and selectivity in order to maximize the membrane efficiency and to provide directions for new membranes or new processes. The polymer concentration is one of the significant factors in determining the membrane performances. Different type of polymer concentration used in the casting solution result in the difference morphology and separation performance in CO_2/CH_4 gas separation. In order to get high purity of methane, so the membrane that exhibit the highest selectivity is needed to achieved the goal.

1.3 OBJECTIVES

The objectives of this study are to develope the asymmetric polysulfone membrane and to identify the concentration of asymmetric polysulfone membrane to produce high selectivity membrane for CO_2/CH_4 gas separation.

1.4 SCOPE OF STUDIES

In order to achieve the set objectives, several scopes of work have been identified.

a. Study of different polymer concentration to produce asymmetric polysulfone membrane.
b. Used gas permeation test to test the develop membrane.
c. Characteristic study of membrane morphology by using Scanning Electron Microscope (SEM).
d. Identify functional group contains in membrane by using Fourier Transform Infrared Spectroscopy (FTIR).

CHAPTER 2

LITERATURE REVIEW

2.1 MEMBRANE SEPARATION PROCESS

A membrane is a permeable or semi-permeable phase, often a thin polymeric solid, which restricts the motions of certain species. Generally, a membrane is a phase or a group of phase that lies between two different phases, which is physically or chemically distinctive from both of them and which due to its properties and the force field applied (driving force), is able to control the mass transport between these phases (Paul and Yampol, 1994). In simple words, membrane can be defined as a barrier between two fluids, which allows selective transfer of some species through a driving force.

According to Pabby (2008), membranes can be classified as homogeneous or heterogeneous, symmetrical or asymmetrical, and porous or non- porous. Besides, they can be organic or inorganic, liquid or solid. There are three different types of pore size classifications: microporous ($dp < 2nm$), mesoporous ($2nm < dp < 50nm$) and macroporous ($dp > 50nm$) (Mccusker and F. Liebau, 2001).

The historical development of membrane has started at eighteenth century. Membrane technology has been developed from a laboratory technique to a large-scale industrial application. Today membrane technology is applied in a wide range of applications such as in water purification, food industry, dairy, pharmaceutical, textile industry, petrochemical industry and many other applications. Table 2.1 shows some early contributions in the development of membrane.

Table 2.1: Early contributions in the development of membrane (Cardew and Lew, 1994)

Contributions	Membrane Process	Contributors	Years
Observations	Osmosis	Nollet	1748
	Electro osmosis	Reuss, Porret	1816
	Dialysis	Graham	1861
Relations	Diffusion	Fick	1885
	Osmotic pressure	Van't Hoff	1887
	Electrolyte transport	Nernst Planck	1889
Theoretical considerations	Osmotic pressure	Einstein	1905
	Membrane potentials	Henderson	1907
	Membrane equilibrium	Donnan	1911
	Anomalous osmosis	Sollner	1930
	Irreversible thermodynamics	Kedern, Katchalsky	1964
Transport model	Ionic membrane	Teorell	1937
	Pore model	Schmid	1950
	Solution diffusion model	Lonsdale	1965

Transport of selected species through the membrane is achieved by applying a driving force across the membrane. This gives a broad classification of membrane separations in the way or mechanism by which material is transported across a membrane. The flow of material across a membrane has to be kinectically driven, by the application of either mechanical, chemical or electric work. The driving forces are either pressure, concentration, temperature potential. In many cases the transport rate (permeation) is proportional to the driving force and the membrane can be categorized in terms of an appropriate permeability coefficient. The use of driving force as means of classification is not altogether satisfactory because apparently different membrane process can be applied for the same separation, for example electrodialysis, reverse osmosis and pervaporation in the desalination of water. All the process use membrane which are micropous in nature.

There are the most simple form of membrane regarding mode of separation and consist of solid matrix with defined pores ranging from 100nm to 50µm in size. Table 2.2 lists the membrane processes and the driving force.

Table 2.2: Membrane separations and materials (Matsuura, 1996)

Process	**Application**	**Driving Force**
Microfiltration	Separation of suspended particles.	Hydrostatic pressure
Ultrafiltration	Concentration and purification of solvents from macromolecular solutions.	Hydrostatic pressure
Nanofiltration	Concentration and purification of solvents from medium molecular weight solutes.	Hydrostatic pressure
Membrane distillation	Desalination and concentration of solutions.	Temperature
Electro dialysis	Desalination and deacidification.	Electric potential
Reverse osmosis	Desalination, concentration of low molecular weight solutes.	Hydrostatic pressure
Gas permeation	Gas separation	Hydrostatic pressure Concentration gradient
Pervaporation	Separation of azeotropes and liquid mixtures.	Concentration gradient Vapor pressure
Liquid membranes	Separation of ions and solutes from liquids.	Concentration Reaction

Nowadays, membrane technology is becoming an established part of several industrial processes. The technology is largely applicable in the food industry, in the manufacture of dairy products and in the gas processing industries. Membranes important in water industry and avoid people from suffering kidney disease. The markets of membrane in Asia and South America are growing fast. According to study, hemodialysis/hemofiltration alone had sales of over US 2200 million in 1998.

Reverse osmosis (RO), ultrafiltration (UF) and microfiltration (MF) had sales over 1.8 billion dollars respectively in 1998. Membranes and modules were sold for US 400 million each year world wide for use in reverse osmosis. Ultrafiltration membranes and modules brought about US 500 million insales in 1998 with an expected growing rate of 10% a year. Sales of microfiltration equipment and membrane is 2.5 billion in 2008. Gas separation accounted for about US 230M. (Nunes *et al*, 2006). Figures 2.1 below shows the membrane and the types module sales according to the application used.

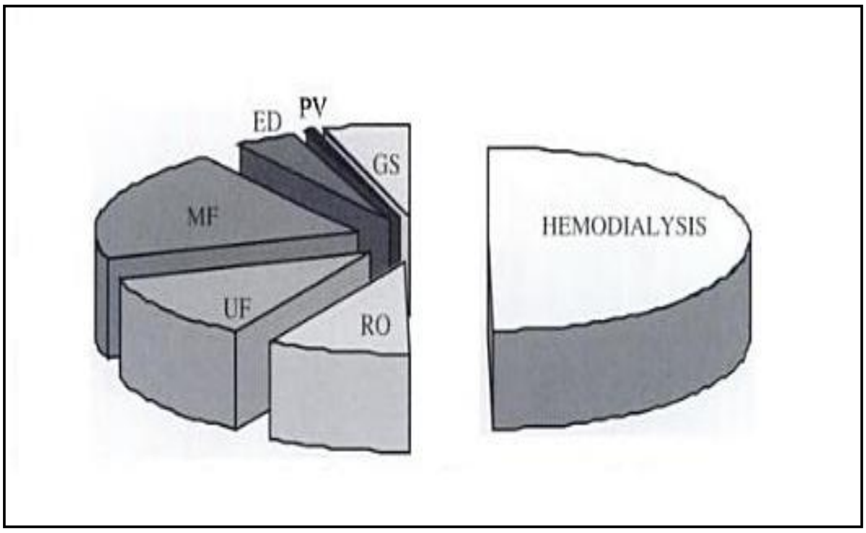

Figure 2 .1: Membrane and Modules sales for different process application (Nunes *et al*, 2006)

2.2 TYPES OF MEMBRANE PROCESS

2.2.1 Ultrafiltration

Ultrafiltration (UF) is the process that involved the separating of small particles and dissolved molecules from fluids. The process separation is depends on molecular size. The molecules with the same size can not be separated by ultra filtration. The range of materials from 1K to 1000K molecular weight (MW) is retained by certain ultrafiltration membranes, while salts and water will pass through. Colloidal and particulate matter can also be retained. Materials that is significantly smaller than the pore size rating pass through the filter and can be depyrogenated, clarified and separated from high molecular weight contaminants. Materials larger than the pore size rating are retained by the filter and can be concentrated or separated from low molecular weight contaminants. Usually, the process of ultrafiltration is involved in the proteins separating from buffer components for buffer exchange, desalting, or concentration. Ultrafilters are also practicalin the process of removing or exchange of sugars, non-aqueous solvents, the separation of free from protein-bound ligands, the removal of materials of low molecular weight, or the rapid change of ionic and/or pH environment (Munir, 2006).

2.2.2 Microfiltration

Micro filtration (MF) is the process of removing particles or biological entities in the range of 0.025 μm to 10.0μm by passage through a microporous medium such as a membrane filter. Membrane filters has been used for final filtration. Membrane and depth filters offer certain advantages and limitations. They can complement each other when used together in a microfiltration process system or fabricated device. The retention boundary defined by a membrane filter can also be used as an analytical tool to validate the integrity and efficiency of a system. Microfiltration also can be used in sample preparation to remove intact cells and some cell debris from the lysate. For this type of separation, the membrane pore size cut-offs used are typically in the range of 0.05 μm to 1.0 μm (George, 2009).

2.2.3 Reverse Osmosis

Reverse osmosis (RO) is the process of separating salts and small molecules from low molecular weight solutes (typically less than 100 daltons) at relatively high pressures using membranes with NMWLs of 1 kDa or lower. RO membranes are normally rated by their retention of sodium chloride while ultrafiltration membranes are characterized according to the molecular weight of retained solutes. Millipore water purification systems employ both reverse osmosis membranes as well as ultrafiltration membranes. Reverse osmosis systems are primarily used to purify tap water to purities that exceed distilled water quality. Ultrafiltration systems ensure that ultrapure water is free from endotoxins as well as nucleases for critical biological research (Munir, 2006). The commercialization of membrane technology and the date commercialize is summarized in table 2.3.

Table 2.3: Approximate date for commercialization of membrane technology for various applications (Perez and Zhang, 1997)

Technology	Industrial application	Commercialization
Electrodialysis	Desalination of Brackish water	1952
Reverse Osmosis	Desalination of Brackish/ sea water	1965
Ultrafiltration	Paint Recovery (Electrocoat)	1965
Electrosynthesis	Chlorine / caustic production	1972
Gas separation	Hydrogen recovery	1979
Pervaporation	Alcohol removal from water	1979
Nanofiltration	Softening of hard water	1990
Microfiltration	Filtration of potable water	1994

2.3 MEMBRANE MODULE

In industrial application of membrane process, large surface areas are required. A practical solution for providing this large surface area is packing the membranes into a small unit call module. The typical of membranes module that largely used for industrial application such as plate and frame module, spiral wound module, tubular module and hollow fiber module.

2.3.1 Plate and Frame Module

This type of module is a simplest structure and easy for membrane replacement. General advantages of this module include low volume hold-up per unit membrane area (attractive for recovering valuable biological) and the ability to process highly viscous solution because of the thin channel height (0.3 – 0.6 mm) (Belfort, 1988). This design provides a configuration which is closest to the flate membranes used in the laboratory. Sets of the two membranes are placed in a sandwich-like with their feed sides facing each other. In each feed and permeate compartment thus obtained a suitable spacer is placed. The numbers of sets needed for a given membrane area furnished with sealings rings and the two end plates then builds up to a plate and frame stack.

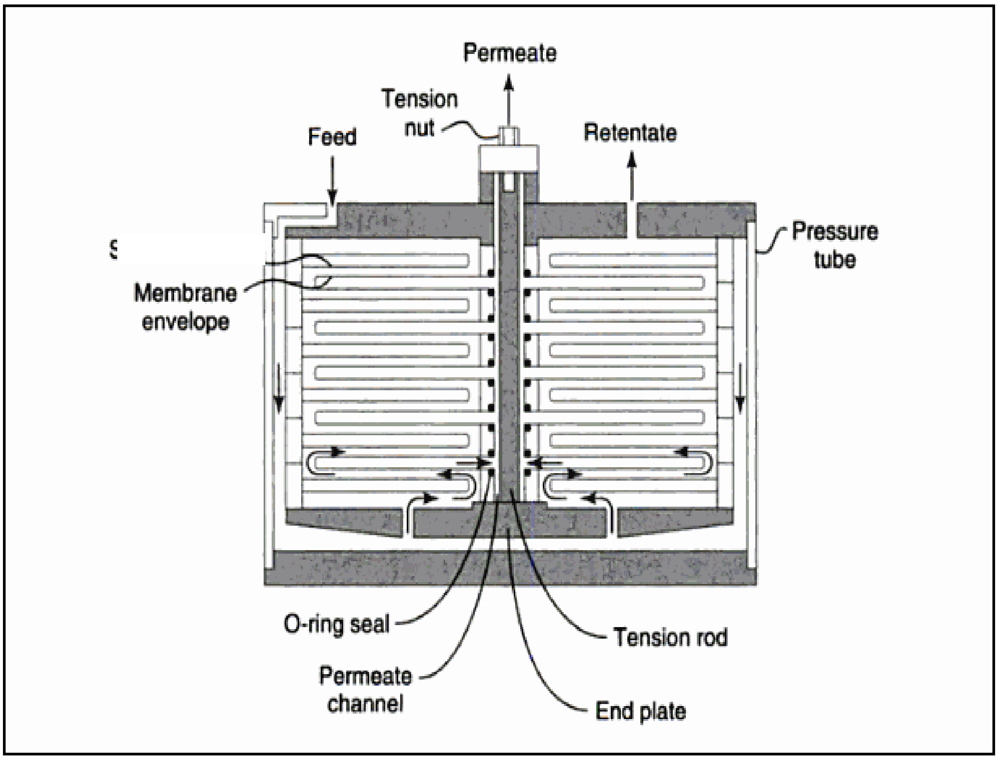

Figure 2.2: Schematic of the plate and frame module (Baker, 2000)

2.3.2 Tubular Module

In this type of module, a number of membrane of tubular shape are encased in a container. The feed solution always flows through the center of the tubes while the permeate flows through the porous supporting tube into the module housing. Ceramic membranes are mostly assembled in such tubular module configurations. Tubular module is convenience membrane replacement and easy cleaning of surface contamination. Besides, the energy consumption is high according to per unit amount of liquid treated.

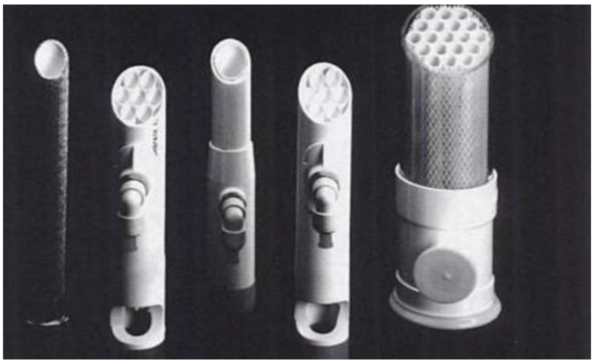

Figure 2.3: Tubular module for ultrafiltration

Tubular module commonly used in ultrafiltration application since this module is resistance to membrane fouling and exhibits good hydrodynamics, resulting in lower cost of production. This module is non-self supporting membrane but it have supported by a tube from outside. The flow in tubular membrane is inside out since the location of tubular membrane is inside a tube. Large numbers of tubes are manifolded in series. The feed fed through all the tubes connected in series, typically at high velocity with typical operating pressures of 20 to 80 psi, which is sufficient to maintain turbulent flow. Clean fluid passes through the pores membrane, while suspended particulates remain in the retentive stream. Permeate is removed from each tube and sent to a permeate collection header. The turbulent flow of the retentive stream prevents the cake formation on the inner surface of the tube resulting high flux and longer shelf life (Prasad, 2010).

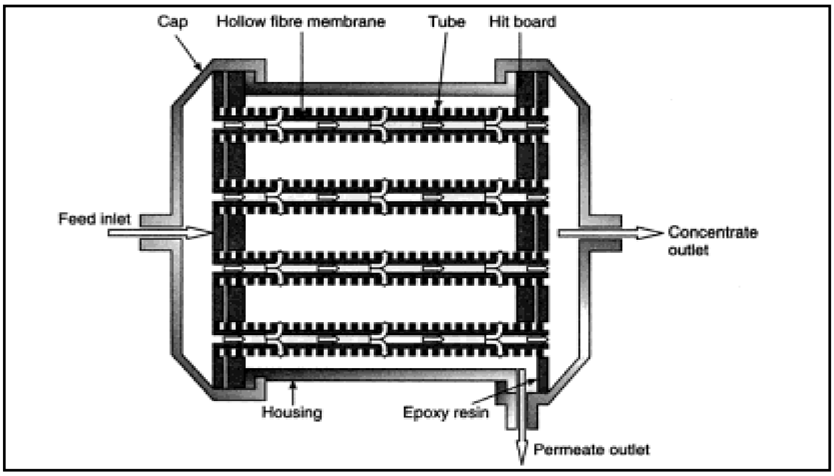

Figure 2.4: Schematic diagram of tubular module

2.3.3 Hollow Fiber Module

Hollow fiber module consists of a large number of fibers assembled together in a module. The free ends of the fibers are often potted with agents such as epoxy resins, polyurethanes, or silicon rubber. The membranes are self supporting for this module. There are two basic types of arrangement for this module :

1) Inside out where the feed solution passes through the bore of the fiber and the permeate is collected on the outside of the fiber.
2) Outside in where the feed solutions enters the module on the shell side of the fibers and the permeate passes into the fiber bore.

The choice between the two concepts is mainly based on some parameters such as operation pressure, pressure drop or type of membrane available. The hollow fiber module is often used when the feed stream is relatively clean, such as in gas separation and pervaporation. It has also been use for desalination process, but treatment is need.

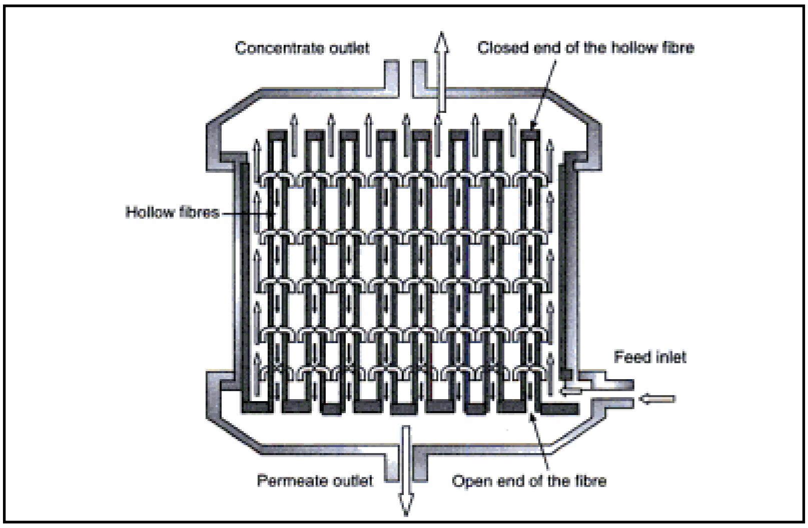

Figure 2.5: Schematic representation of shell side feed type hollow fibre membrane module

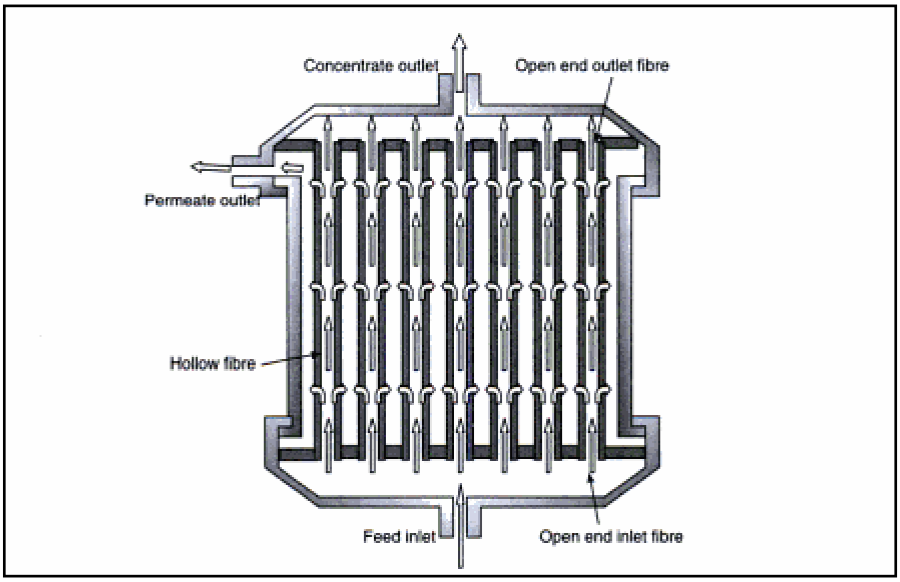

Figure 2.6: Schematic representation of bore side feed type of hollow fibre membrane module

Hollow fibre membrane modules are available in two basic geometries such as shell side feed design (figure 2.4) and bore side design (figure 2.5). In shell side module, the system is pressurized from the shell side driving permeate through a closed bundle of fibres contained in a pressure vessel, and permeate exits through the open fibre ends. The shell side module is simple, easy and economic. In bore side feed type of hollow fibre module, units are open at both ends for inlet and outlet, and the feed fluid circulates through the bore of the hollow fibres. The pressure drop inside the hollow fibers is reduced by increasing the diameter of the fine fibers and spinning compared to the shell side feed system (Nath, 2008).

2.4 ADVANTAGES OF MEMBRANE TECHNOLOGY

There are many reasons why numerous fluid separation markets have adopted membrane separation technologies in such a short time. But the most significant reason is that they are more efficient than traditional technologies.

2.4.1 Energy Saving

Energy savings are among the main reasons for selecting membrane technologies. In food processing application, the compact system of membrane can operate at near room temperature, so at the same time, the cooling cost will be reduced. In waste water industries, the usage of membrane will improves wastewater management, aiding the reclamation of salable by-products from waste streams in the food processing businesses. Besides, membrane separation has been recognizing as the energy saving technology and high quality of production.

2.4.2 Clean Energy

The development of advanced technology in membrane separations gives significant effect in the energy and environmental concern. The continuous use of fossil fuels for transportation, as primary energy sources and indiscriminate use of fossil fuel will cause considerable harm to environment. To prevent this from damage, scientists have been actively working on upgrading membranes for fuel cells, which are expected to compete with petroleum-based energy sources particularly in the transportation markets. These enhanced membranes will not only improve hydrogen production for use as a fuel in vehicles, but will also sequester carbon dioxide to reduce the greenhouse effect and global warming due to burning of fossil fuels. Research in membranes for the energy and environmental markets is particularly intense for fuel cell membranes, hydrogen separation, and carbon dioxide recovery from fossil fuel applications.

2.4.3 The Ability of Connection to Other Processes

To meet the complex demands in fluid separation, membrane technologies can be combined with each other and with other separation technologies. The example of applications that is classified as the challenging application is in the treatment of seawater and brackish water sources and wastewater recovery. Pretreatment with ultra or micro-filtration followed by reverse osmosis is being used for desalination to minimize fouling. In the treatment of wastewater with organic matter, membrane bioreactors are well accepted in many parts of the world.

2.4.4 Good Weight and Space Efficiency

Skid construction can be optimized to the space available, and multiple elements can be inserted into tubes to increase packing density. The space efficiency that is shows in membrane technology is important especially in the limited area of plant such as for offshore environment, where deck area is at a premium, and is the reason why so many new offshore developments have chosen to use membranes for acid gas removal.

2.4.5 Lower Capital Cost

The scope, cost, and time taken for site preparation are minimal since membrane systems are skid mounted, except for the larger pretreatment vessels. Therefore, installation costs are significantly lower than alternative technologies, especially for remote areas. Furthermore, membrane units do not require the additional facilities, such as solvent storage and water treatment, needed by other processes.

2.4.6 Operational Simplicity and High Reliability

Because single-stage membrane systems have no moving parts, they have almost no unscheduled downtime and are extremely simple to operate. They can operate unattended for long periods, provided that external upsets, such as well shutdowns, do not occur. Items in the pretreatment system that could cause downtime, such as filter coalescers, are usually spared so that production can continue while the item is under maintenance. The addition of a recycle compressor adds some complexity to the system but still much less than with a solvent or adsorbent-based technology. Multistage systems can be operated at full capacity as single-stage systems when the recycle compressor is down, although hydrocarbon losses will increase. The start-up, operation, and shutdown of a complex multistage membrane system can be automated so that all important functions are initiated from a control room with minimal staffing (Dortmundt and Doshi, 1999).

2.47 Lower Operating Costs

The only major operating cost for single-stage membrane systems is membrane replacement. This cost is significantly lower than the solvent replacement and energy costs associated with traditional technologies. The improvements in membrane and pretreatment design allow a longer useful membrane life, which further reduces operating costs. The energy costs of multistage systems with large recycle compressors are usually comparable to those for traditional technologies.

2.4.8 Deferred Capital Investment

Often, contracted sales-gas flow rates increase over time, as more wells are brought on-line. With traditional technologies, the system design needs to take this later production into account immediately, and so the majority of the equipment is installed before it is even needed. The modular nature of membrane systems means that only the membranes that are needed at start-up need be installed. The rest can be added, either into existing tubes or in new skids, only when they are required. Even on offshore